

Simulations of NO dissociative adsorption on an atomically thin Cu layer

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Abstract. To investigate chemical reactivity of Cu atomic-scale structures, we performed simulations based on the generalized gradient approximation in the density functional theory. An atomic layer of Cu forming a triangular lattice (TL) was found to give a stable structure. The nitrogen monoxide molecule (NO) was adsorbed on some atomic sites of TL or on an atomic step structure (ASS) of Cu. The molecular adsorption energy on TL was -0.83 eV. Our data suggested that dissociative adsorption of NO with a dissociation energy of -1.08 eV was possible with an energy barrier of order 1.4 eV. In this optimized structure, the nitrogen and oxygen atoms were embedded in the Cu layer. On the step, NO adsorbed at a bridge site and the formation energy of Cu-(NO)-Cu local bond connections was estimated to be around -1.32 eV. Molecular dissociation of NO with a dissociation energy of -0.37 eV was also possible around ASS.

1. Introduction

To enhance chemical reactivity of Cu surfaces with nitrogen oxides (NO_x) is an important issue for development of new catalytic materials effective in the NO_x reduction process [1, 2]. The dissociative adsorption of NO_x , for example, was found to be less expected on Cu, compared with highly reactive Rh, Ir, Ru, Co, and Ni surfaces, although dissociative adsorption was reported at finite temperatures in experiments [3, 4]. In order to provide active surfaces for NO dissociation, Cu thin films and low index surfaces were considered on one hand [5, 6, 7, 8]. In several electronic structure calculations based on the density functional theory (DFT), on the other hand, dissociative adsorption of NO was found to be possible but energetically un-favored compared with molecular adsorption [9, 10, 11, 12].

We note that the simulations were often performed with respect to reactions on stable bulk surfaces. Although the theoretical data suggested less reactivity of Cu bulk surfaces for NO_x reduction, there could be remarkable reactivity on some surface-like atomic structures of Cu. When we considered wider classes of nano-scale structures other than defined surfaces of bulk Cu crystals, one could find another clue. In this line of approach, indeed, many theoretical investigations with computer simulations had been done intending to explore efficiency of *e.g.* step-like structures of various metals [13, 14, 15, 16, 17, 18, 19, 20, 21].

To explore possible NO dissociation, we consider ultra thin Cu structures. In this study, we focus on a Cu atomic layer, that is the triangular lattice of Cu. We adopted structural optimization simulations based on electronic structure calculations to find a stable Cu triangular lattice (Cu-TL). On this thin structure, we adsorbed an NO molecule and performed an optimization simulation. After finding molecular adsorbed structures, we searched possible dissociative adsorption on the Cu structures. To find a possible reaction path and to conclude a reduction process, we performed simulations for reaction path estimation. In the discussion of this paper, by comparing the obtained adsorption energies with each other, we will discuss a possible NO_x reduction mechanism by using Cu nano-structures.

2. Methods

We adopted the electronic structure calculation based on the density functional theory [22, 23] to estimate the electronic state, and to obtain inter-atomic forces. In this simulation, the Kohn-Sham wavefunctions were expanded in the plane-waves and the electron charge density was given both on a real space mesh and on the Fourier mesh. An approximation for the exchange-correlation energy functional by Perdew, Burke, and Ernzerhof [25, 26] in the scheme of the generalized gradient approximation was adopted. The ultra-soft pseudo-potential [27] was utilized to describe the valence electron state. All of our simulations were done using the simulation package, the Quantum ESPRESSO [24].

The calculation conditions are summarized as follows. The energy cut-off for the wave function expansion was 30 [Ry], while the cut-off for the charge density was 240 [Ry]. The Brillouin zone integration was done using a k mesh of $8 \times 8 \times 1$ for the largest super cell adopted. These values were refined, if the computation facility allowed much accurate calculations. The convergence criterion for the force constant was that the simulation ended, when the absolute value of the total force vector became less than 1×10^{-3} [Ry/a.u.].

3. Atomic layer of Cu

To explore possible high reactivity of Cu nano-structures, we considered atomic-layer structures. An important structure for our discussion is the Cu triangular lattice (Cu-TL). In this section, we show data for structural and electronic properties of Cu-TL.

3.1. Atomic structure

We obtained an optimized lattice structure using a Cu atomic layer in a primitive super cell. Major calculation conditions were the same as those given in Section 2. The k -point mesh was $24 \times 24 \times 1$ in this simulation. The cell was given in a hexagonal structure. The vacuum layer had thickness of 15 Å. In this simulation, the value of the lattice constant was optimized. The bond length was found to be 2.43 Å. (Fig. 1) This value is rather small compared to the bond length 2.55 Å of the bulk fcc Cu. The reason for shrink in the bond length is mainly to reduce the total band energy. The total energy of TL was energetically higher than the bulk Cu by 1.2 eV per a Cu atom.

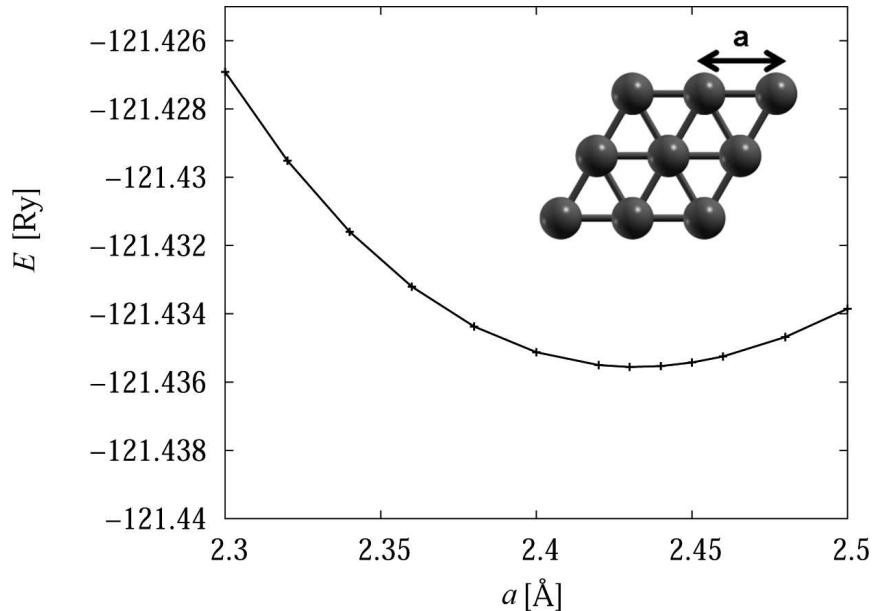


Figure 1. The total energy E of the triangular lattice of Cu. The value of E in Rydberg is given as a function of the lattice constant a [Å].

Starting from some initial conditions, we found appearance of Cu-TL in optimized structures. As another evidence to show the local stability of Cu-TL, we considered an atomic two-layer structure (ATLS). This structure was obtained by cutting the bulk fcc Cu crystal and was placed in a simulation super-cell. The layer structure was perpendicular to the (100) direction of bulk Cu and thus was contained in an orthorhombic unit cell. Energy difference between ATLS and Cu-TL was 3.11 eV per a Cu atom. An optimization calculation of the structure concluded local stability. But, ATLS was not kept against global reconstruction which was happened when an NO molecule was adsorbed on it. Furthermore, we found a strongly reacted structure starting from an NO molecule adsorbed on ATLS. It means that using ATLS as an initial structure, naively speaking, we realized simulated annealing in our simulation. Compared with this un-stable structure, Cu-TL was found to be stable. Once the molecule was adsorbed on ATLS, reconstruction of ATLS happened and formation of Cu-TL was observed in our simulations. Conversely, we can say that Cu-TL is stable against distortion making corrugation toward ATLS.

Even when one observed local stability of an atomic structure in simulation, however, a final evidence of the structure would be requested to be given using real experiments. Realization of an atomically thin layer, *i.e.* Cu-TL, will need development of a fabrication method. Recently, formation of an atomic layer of Pb on the Si(111) surface was reported [28]. In this superconducting Pb system, positions of Pb atoms are affected by the atomic structure of the substrate and inter-atomic distance between Pb atoms is not determined independently from the substrate. The most remarkable example of natural realization of the atomic layer is graphene [29, 30]. This unique flexible structure of carbon is possible to be supported in air according to the strong C-C sp^2 bonding. Peeling a graphene sheet and pasting it on a silicon-di-oxide surface, graphene is obtained efficiently from graphite.

In case of Cu, we may expect formation of an atomic layer on a suitable inert substrate. We might be able to keep the atomic layer as a film pasted on a support with a nano-meter-scale hole. Then, mechanical properties of the atomic layer would be paid attention like a graphene sheet [31]. But for our consideration of NO adsorption, a local structure of Cu is important. So, we assume an atomic-scale local structure in a part of nano-scale Cu.

3.2. Electronic structure

The density of states (DOS) of Cu-TL is shown in Fig. 2. The major peaks are characterized similarly to the bulk copper. Looking DOS from the low energy region, we see that the 4s band starts from -6.38 eV and spreads over above the Fermi energy. Sharp peaks of 3d levels are seen from -4.04 eV but the 3d bands end below the Fermi level. Thus, perfectly filled 3d band with the $(3d)^{10}$ configuration is kept and the structure behaves as an *s* metal. These characteristic features are seen in the electronic band structure of Cu-TL, too. (Fig. 3) Along the Γ -M line, or the K- Γ line, we see

hybridization of the 4s band and a 3d band.

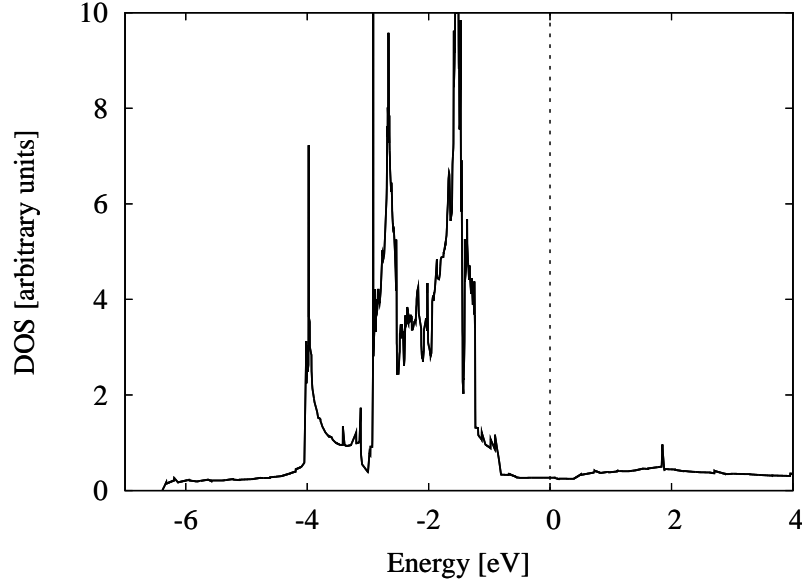


Figure 2. The electron density of states of the triangular lattice of Cu.

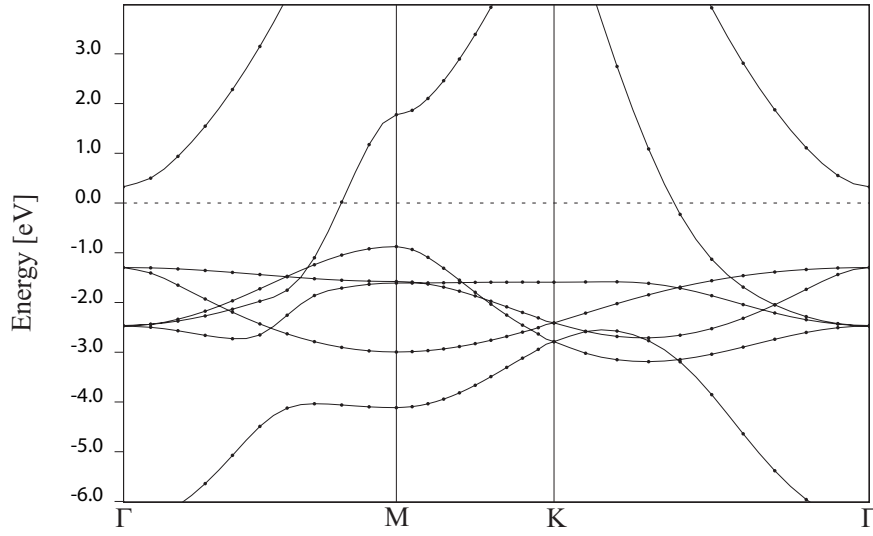


Figure 3. The Kohn-Sham band structure of the Cu triangular lattice.

Comparison with the Cu (111) surface allows us to evaluate similarity and difference between Cu-TL and the bulk Cu surface. The density of states in the 4s band leveled almost around 0.2 owing to two-dimensional nature. DOS in the 3d bands peaked well above 10 for Cu-TL in the unit of states/eV per a unit cell, while the value is from 4 to 6, except for a singularity at the top of the 3d bands, for the Cu (111) surface. The shorter bond length of Cu atoms, the height in DOS should be lower in a fixed lattice

structure. Thus, the higher DOS peak for Cu-TL than for the bulk Cu suggests that two-dimensional nature of Cu-TL affects DOS.

Since DOS at the Fermi level is almost the same for both Cu-TL and the Cu (111) surface, the chemical reactivity of NO is expected to be similar, if the structure is kept undeformed. However, we should note that the top of Cu 3d bands is much closer to the Fermi energy for Cu-TL than the Cu (111) surface. This tendency suggests higher reactivity of Cu-TL against NO.

When the stable adsorption site is the on-top site, similarity in characteristic energy like the adsorption energy would be expected. However, if a bridge site or a hollow site became stable for NO on Cu-TL, we could have difference even in the chemical reactivity from that on the Cu (111) surface. This is because much easy deformation of the Cu network structure is expected for Cu-TL and the bond formation between NO and Cu-TL will create distortion. In the next section, we discuss occurrence of strong reactions between NO and Cu-TL.

4. Adsorption of NO

We consider adsorption of NO on Cu-TL and an atomic step like structure (ASS) created on an Cu atomic layer. The second structure was found in optimization simulations of NO adsorption on ATLS. Observing results of NO-adsorbed structures starting from ATLS, we identified a stable substrate structure in a super cell as Cu-TL with ASS in our simulations. Therefore, we regarded Cu-TL and ASS as typical atomic-scale layer structures of Cu. Several characteristic adsorption sites for NO were found on these structures.

4.1. Adsorbed structures

Molecular adsorbed structures were obtained by structural optimization. Starting from an initial structure with a NO molecule a little separated from a substrate, Cu-TL, ASS or ATLS, each adsorbed structure was determined. By a series of simulations, we found the next general rules for molecular adsorption. On Cu-TL, adsorption on a hollow site is energetically most favorable. On ASS, a bridge site on the Cu array is energetically most favorable among sites including an on-top site, a hollow site in the back surface, and a bridge site in the back surface. Thus, we treat these locally stable structures only in the following discussion.

While, structures corresponding to dissociative adsorption were given by locating N and O atoms a little separated on the substrate and by optimizing the whole structure. We have found two locally stable dissociative adsorbed structures on Cu-TL and on ASS. The structures are depicted in Fig. 4. As typical structures, we consider these structures only.

We define the adsorption energy by the next formula.

$$E_{ad:NO} = E_{Cu-NO} - E_{Cu} - E_{NO}, \quad (1)$$

$$E_{ad:N,O} = E_{Cu-N,O} - E_{Cu} - E_{NO}. \quad (2)$$

Here, $E_{ad:NO}$ is the molecular adsorption energy, while $E_{ad:N,O}$ is the dissociative adsorption energy. The values of E_{Cu-NO} and $E_{Cu-N,O}$ are the total energy of a Cu slab with NO and that of another slab with a N atom and an O atom adsorbed on the Cu slab, E_{Cu} is the total energy of a Cu slab without NO, and E_{NO} is the total energy of the NO molecule contained in a super cell with the same size as the other calculations. Molecular dissociation energy is defined as,

$$E_{diss} = E_{ad:N,O} - E_{ad:NO}. \quad (3)$$

Adsorbed structures found in our simulations are itemized in the next list. The adsorption energy is also shown in each parenthesis for convenience.

molecular adsorption on Cu-TL In adsorption of a NO molecule on a surface of Cu-TL, a hollow site (-0.83 eV) is selected. See the center figure of Fig. 4 (a).

molecular adsorption on ASS In adsorption of a NO molecule on an atomic step-like structure, a bridge site (-1.32 eV) is selected. See the center figure of Fig. 4 (b).

dissociative adsorption Dissociative adsorption of NO is found on TL (-1.92 eV) and on ASS (-1.69 eV). See the right figures of Fig. 4 (a) and (b).

Now, dissociative adsorption structures are discussed. We have two typical dissociative adsorption structures on Cu-TL and on ASS. In the first structure, the nitrogen atom locates at a center of five surrounding Cu atoms. (See the right figures of Fig. 4 (a).) This structure may be regarded as a nitrogen interstitial impurity in a Cu lattice. Arrangement of Cu is largely distorted from pure TL, so that the N atom is embedded in Cu layer. The oxygen atom locates at a hollow site and it is embedded in Cu layer. The local structure of these impurity sites are NCu_5 and OCu_4 . Here, the OCu_4 structure is planer.

A reason for appearance of the high coordination numbers for N and O is that Cu valence is not largely modified and that $3d^{10}$ configuration is almost kept. 4s electrons are in extended states so that the local N^{-3} and O^{-2} are efficiently screened by neighboring five and four copper atoms.

On SS, we have another dissociative adsorbed structure for NO. The nitrogen atom is again embedded in the Cu structure. (See the right figure of Fig. 4 (b).) In this structure, the oxygen atom is at a bridge site and keeps two-fold coordination, while the nitrogen atom has four-fold coordination.

Now we compare the obtained values of adsorption energy with those in the literature. The molecular adsorption energy is higher for ASS than those on Cu-TL. Except for a case of a bond-center site on the back surface of ASS, molecular adsorption favors the bridge site of the step-like structure. This general tendency is natural in comparison to the other examples known in the literature.

The most notable feature of our results is the finding of the large dissociative adsorption energy. We conclude that the dissociative adsorption may happen, when the

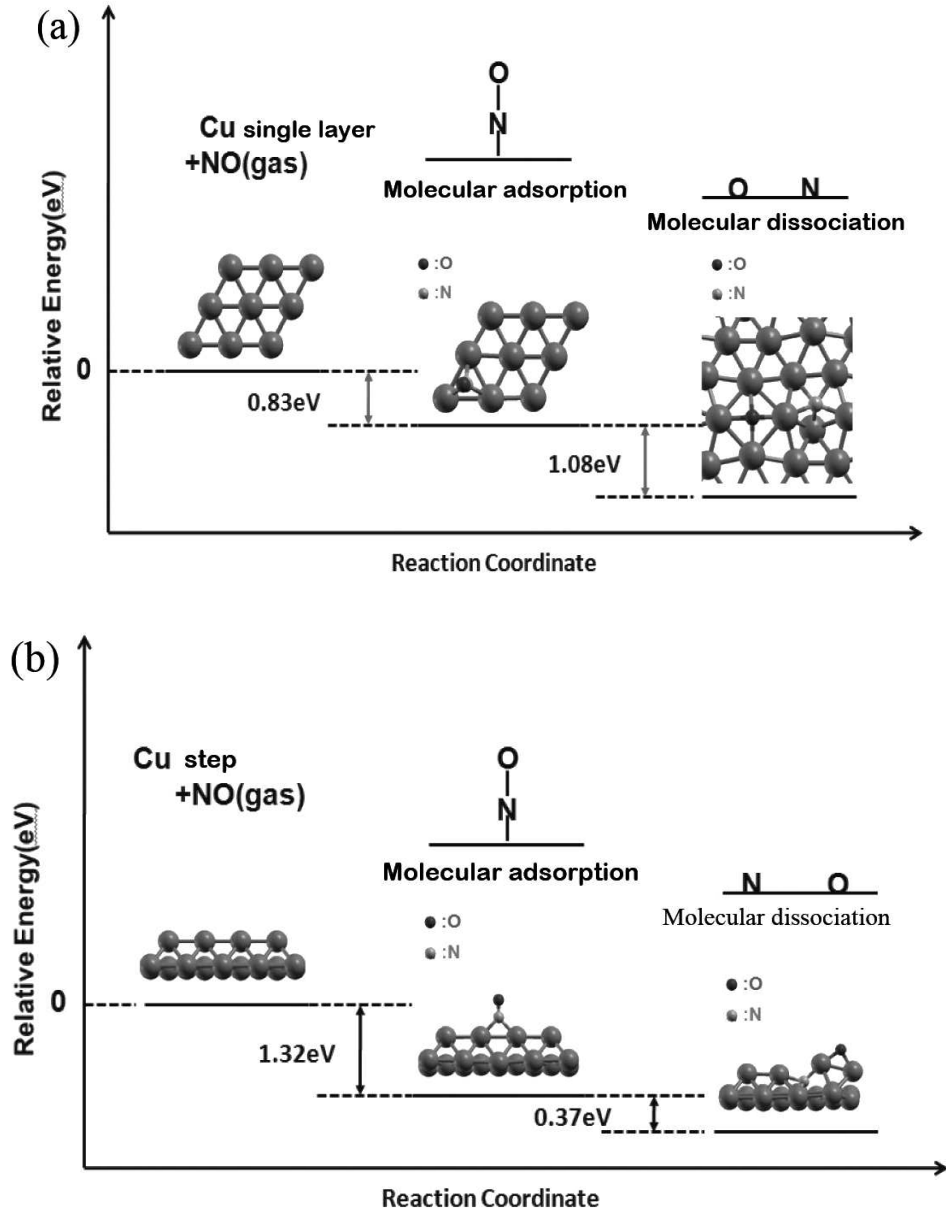


Figure 4. The energy diagram of NO adsorbed structures on a Cu atomic layer in (a) the triangular lattice and in (b) a layer with an atomic step-like structure.

nitrogen atom can go to an interstitial site of a Cu structure. The large value of $E_{ad:N,O}$ (-1.92 eV on TL and -1.69 eV on ASS) is actually possible, since these structures possess high coordination of Cu around the nitrogen atom.

On the clean Cu (111) surface, NO favors the molecular adsorption (with the adsorption energy of -1.22 eV estimated in Ref. [10]) against the dissociation of NO, where the dissociative adsorption energy is estimated to be -0.79 eV in Ref. [10]. The qualitative difference between data for known bulk surfaces and our result should be attributed on movement of Cu atoms in the reconstruction process. In our simulation,

positions of Cu atoms are rather easily modified because the atomic structure of Cu is just a single layer. Even in the optimization simulation, we can reach the nitrogen insertion in the Cu structures.

From the present result, we conjecture the following picture. If a Cu structure allows large configurational distortion owing to the chemical reaction with NO, the nitrogen atom can move into the Cu structure and form the local NCu_m configuration. ($m = 4$ or 5 .) Owing to the energy reduction coming from the large formation energy of the local NCu_m structure, we can expect even the dissociative adsorption of NO on Cu. In the real Cu nano-structures, there can happen large distortion of Cu configuration owing to finite temperatures and possible local strain. Therefore, our simulation, which is prepared using the atomic layer of Cu, might have derived a hidden possible path of the NO dissociative adsorption on Cu structures.

4.2. Reaction path estimation of molecular dissociation

To estimate a reaction path on the NO reduction on Cu-TL, we estimated the local structure and the energy of a transition state using the nudged-elastic-band method. The initial configuration was the molecular adsorbed structure on Cu-TL and the final configuration was the dissociative adsorbed structure obtained in §4.1. The dissociation reaction was determined by obtaining the transition state with an energy E_{TS} for the NO reduction process.

The activation energy for dissociation of NO on the atomic layer is estimated using the next definition.

$$\Delta E_{diss} = E_{Cu-NO} - E_{TS}. \quad (4)$$

An upper bound of the transition potential barrier is estimated to be 1.4 eV. In the initial state, the NO molecule adsorbed on Cu-TL with the nitrogen atom binding to the Cu surface. In the transition state, the oxygen atom had local bond connections with surrounding Cu atoms to reduce the total energy. To form this distorted structure in the transition state, the whole Cu atomic configuration were optimized, creating drastic change in Cu-TL.

5. Summary and Conclusion

Utilizing the DFT-GGA simulations, we have shown that NO dissociative adsorption may happen on an atomic Cu layer, which is the triangular lattice of Cu atoms (Cu-TL). The reactivity of Cu-TL against molecular adsorption of NO was found to be similar to the Cu(111) surface. Some stable sites for NO were found to give molecular adsorption. However, our optimization simulation revealed that there was a co-adsorbed structure of N and O atoms, which was energetically stabler by 1.08eV than the molecular adsorbed Cu-TL structure. A reaction path estimation showed existence of a path with an energy barrier of 1.4eV. Thus, we may conclude molecular dissociation of NO on the Cu atomic

layer. The large dissociation energy appears owing to formation of local N-Cu or O-Cu bondings and creation of local N-Cu_n and O-Cu_m structures.

We further considered an atomic step-like structure (ASS) of Cu, which was an atomic-scale wrinkle in the Cu-TL structure. The absolute value of the molecular adsorption energy on the step was larger than the values found for Cu-bulk surfaces or Cu-TL. Our simulation revealed that there existed a dissociative adsorbed structure in which a nitrogen impurity site embedded in a Cu structure was created. The estimated dissociation energy of NO became -0.37 eV on ASS.

Flexibility against modification of this Cu atomic structure in the nano-meter scale is decisive both to stabilize dissociative adsorption of NO and to reduce the energy barrier on the NO-reduction path. Catalytic activity of Cu to reduce NO should appear on the atomically flexible Cu networks. Therefore, in order to realize Cu-based NO_x reduction catalysts, it is important to create atomic structures of Cu, *i.e.* atomic layers, atomic scale clusters, and atomic scale networks, which allow conformational change.

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